# Sorption Characteristics of Polycyclic Aromatic Hydrocarbons in Aluminum Smelter Residues

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High temperature carbon oxidation in primary aluminum smelters results in the release of polycyclic aromatic hydrocarbons (PAH) into the environment. The main source of PAH are the anodes, which are composed of petroleum coke (black carbon, BC) and coal tar pitch. To elucidate the dominant carbonaceous phase controlling the environmental fate of PAH in aluminum smelter residues (coke BC and/or coal tar), the sorptive behavior of PAHs has been determined, using passive samplers and infinite-sink desorption methods. Samples directly from the wet scrubber were studied as well as ones from an adjacent 20-year old storage lagoon and roof dust from the smelter. Carbon-normalized distribution coefficients of native PAHs were 2 orders of magnitude higher than expected based on amorphous organic carbon (AOC)/water partitioning, which is in the same order of magnitude as reported literature values for soots and charcoals. Sorption isotherms of laboratory-spiked deuterated phenanthrene showed strong (~100 times stronger than AOC) but nonetheless linear sorption in both fresh and aged aluminum smelter residues. The absence of nonlinear behavior typical for adsorption to BC indicates that PAH sorption in aluminum smelter residues is dominated by absorption into the semi-solid coal tar pitch matrix. Desorption experiments using Tenax showed that fresh smelter residues had a relatively large rapidly desorbing fraction of PAH (35–50%), whereas this fraction was strongly reduced (11–16%) in the lagoon and roof dust material. Weathering of the coal tar residue and/or redistribution of PAH between coal tar and BC phases could explain the reduced availability in aged samples.

## Introduction

High polycyclic aromatic hydrocarbons (PAH) emissions have been associated with primary aluminum smelters based on the Söderberg technology. In Norway, more than 40% of the total annual PAH emissions is related to the aluminum industry (*1*). Because of more stringent environmental legislations, smelters based on the Söderberg technology will have to be modified or phased out (*2*). This will reduce the amount of PAH emitted from aluminum smelters to the

environment. However, not much is known about the long-term environmental consequences of the large amounts of smelter residues present in the environment.

Aluminum smelters are based on the Hall–Héroult process, where alumina ($Al_2O_3$) is dissolved in molten cryolite ($Na_3AlF_6$) and electrochemically reduced to metallic aluminum using consumable carbon anodes. Such anodes are produced from petroleum coke using coal tar pitch as a binder and can thus be considered as a mixture of solid (coke black carbon, BC) and semi-solid (tar pitch) aromatic carbon materials. In the Söderberg technology, a continuous anode is supplied as a baked anode paste. This high temperature process (970 °C) results in the release of $CO_2$, PAH, and fluorides (*3*).

In the early 20th century, atmospheric release was the main emission pathway of PAH from aluminum smelters (*4*). Water scrubbing of the exhaust fumes, applied since the 1960s, increased the release of smelter soot and PAH to the aquatic environment considerably (*4*). As a result, large emissions of PAH into fjord systems in both North America and Europe have been documented (*4–6*). Annual PAH discharges of several tons of PAH per plant have been estimated (*4*).

Despite high contamination levels in fjord sediments, limited uptake and effects have been registered in benthic organisms (*7*). A large part of the PAH is found to be associated with particulate matter and assumed to be associated with soot particles formed during combustion (*8*).

The role of soot and soot-like materials in controlling the environmental fate of PAH in the aquatic environment has recently received considerable attention reviewed in refs *9* and *10*. Carbonaceous particles from pyrogenic origin (BC), like soot and charcoal, have been shown to sorb PAHs 10–100 times more strongly than amorphous humic organic carbon (AOC).

Generally, BC is a combination of condensed aromatic material (sub-micrometer size) formed in the gas phase (soot) and larger carbonized residues from the original fuel (chars) (*11*). The characteristics of BC may vary depending on the source as well as physical characteristics of the particles (*12*). So far, little has been known concerning the characteristics and sorptive behavior of the carbonaceous material present in aluminum smelter residues. We hypothesize that the carbonaceous material released during different stages of the high temperature aluminum smelting process in Söderberg cells consists of two mixed components: (i) soot and char from incomplete coke combustion and (ii) coal tar from the original anode paste. Condensation reactions in which aggregates of BC and coal tar are formed will take place during cooling and wet scrubbing of the exhaust fumes. PAH may thereby be adsorbed on the BC surface or absorbed in the tar pitch matrix.

In the present study, samples from different stages of the exhaust treatment process have been studied by passive samplers to determine freely dissolved concentrations (*13*) and Tenax infinite-sink desorption (*14*). Samples from wet scrubber sludge (before and after neutralization), airborne dust directly from the smelter roof, and sediment from a 20-year old settling pond adjacent to the smelter were included in the study. The characteristics of the smelter residues are compared to those of well-characterized soot and charcoal samples generated by other processes. This allows assessing the contribution of aluminum smelter residues to the release of PAH in the aquatic environment and helps to determine the risks associated with smelter-impacted sediments.

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## TABLE 1. Chemical Characteristics of Aluminum Smelter Residue Samples Used in This Study

| name | origin | TOC (%) | TON (%) | BC (%) | BC/TOC (%) | PAH[a] (mg/kg) |
|---|---|---|---|---|---|---|
| scrubber | scrubber sludge | 14.1 ± 0.2[b] | 0.15 ± 0.01 | 5.93 ± 0.28 | 42 | 4628 ± 289 |
| scrubber neutralized | scrubber sludge neutralized with calcite | 6.39 ± 0.18 | 0.10 ± 0.01 | 3.06 ± 0.11 | 48 | 2463 ± 108 |
| lagoon | >20 year old settling pond | 28.7 ± 0.2 | 0.42 ± 0.02 | 12.0 ± 0.2 | 42 | 3953 ± 45 |
| roof dust | airborne soot not treated by scrubber[c] | 2.58 ± 0.34 | 0.07 ± 0.00 | 0.64 ± 0.05 | 25 | 518 ± 12 |

[a] Sum PAH content of 16 U.S. EPA priority pollutants. [b] Throughout the table, ± indicates standard deviation in triplicates. [c] Roof sample containing sand and gravel sieved over 250 μm.

## Materials and Methods

**Aluminum Smelter Residues.** Samples of aluminum smelter residues from Söderberg potlines were taken from the roof of the smelter (annotated roof dust), from the wet scrubber before (scrubber) and after acid neutralization with calcite (scrubber neutralized) as well as from sediment of a 20-year old settling pond adjacent to the smelter (lagoon). X-ray diffraction (XRD) measurements (Supporting Information Table S1) revealed that the mineral sample matrix composition consisted of corundum ($\alpha$-$Al_2O_3$) and cryolite ($Na_3AlF_6$) (scrubber and roof dust) or corundum and fluorite ($CaF_2$) after acid neutralization with calcite (scrubber neutralized). Quartz ($SiO_2$) and clay minerals (albite, chlorite, and amphibole) dominated the mineral composition of the lagoon sample.

To determine the BC levels, the Gelinas modification (15) of the chemo-thermal oxidation (CTO) method by Gustafsson (16) was applied. Before thermal oxidation at 375 °C, inorganic carbon was eliminated using hydrochloric acid (HCl, 1 M), and the inorganic aluminum oxide matrix was removed using hydrofluoric acid (HF, 10%). The hydrolyzable organic matter fraction was removed with trifluoroacetic acid (TFA, 6 M), limiting matrix interference and charring risk (15).

Total extractable PAH levels were determined on chemically dried ($Na_2SO_4$) 1–2 g samples by shaking with 10 mL of 75:25 hexane/acetone (24 h) and 10 mL of DCM (48 h).

**Chemicals.** Solvents were Fisher Chemicals Optima quality (Fairlawn, NJ). Naphthalene $d_8$ (NAP), phenanthrene-$d_{10}$ (PHE), anthracene-$d_{10}$ (ANT), and perylene-$d_{12}$ (PER) were from Cambridge Isotope Laboratories (Andover, MA) at >98% purity. Non-deuterated PAH was from various commercial sources. Polyoxymethylene (POM) was obtained in 0.5 mm thick sheets from Vink Kunststoffen BV, Didam, The Netherlands. Tenax TA (60–80 mesh) was obtained from Alltech (Deerfield, IL).

**Aqueous Equilibrium Concentration of Native PAH.** To determine TOC-normalized distribution coefficients ($K_{TOC}$), polyoxymethylene solid phase extraction (POM-SPE) was applied (13) with slight modifications exactly following procedures in ref 17. In short, POM was added to an Al-residue/water system and shaken until equilibrium. Freely dissolved concentrations were subsequently determined directly from the amounts of PAH in the POM using separately determined POM/water distribution coefficients, $K_{POM}$ (L/kg). Triplicate samples (1 g of dry weight), 0.4 g of POM and 250 mL of 0.03 M $NaN_3$ solution (biocide and background electrolyte), were combined in 260 mL all-glass bottles and shaken horizontally (120 rpm; 50 days; room temperature; dark). Equilibration for 28 days has been shown to be sufficient for native PAH in BC samples (17). After equilibration, POM strips were removed and cold-extracted with 10 mL of hexane (48 h; 120 rpm), using NAP-$d_8$, ANT-$d_{10}$, and PER-$d_{12}$ as internal standards (100 ng in 50 μL of hexane). $K_{POM}$ was checked independently for phenanthrene (PHE) and pyrene (PYR) in the same experimental system without sorbent by spiking 50 μL of a stock solution into 1 L of 0.03 M $NaN_3$. The isotherm concentration range was 0.3–160 μg/L PHE and 0.016–8 μg/L PYR. Log $K_{POM}$ values of 3.27 ± 0.03

and 3.74 ± 0.07 were found for PHE and PYR, respectively, not significantly different from earlier reported values (13). For the other PAH, $K_{POM}$ values from literature have been used (13).

**Sorption Isotherm.** To study the linearity of the sorption process, sorption isotherms were determined for laboratory-added PHE-$d_{10}$ following the POM-SPE procedure described previously (18). Sorption was determined on scrubber neutralized and lagoon samples (triplicates at six concentration levels). Samples (70–300 mg dry weight) were filled in 60 mL PTFE-cap vials with 0.012–60 mL of a 500 μg/L PHE-$d_{10}$ solution in 0.03 M $NaN_3$ and 0.2 g of POM. The stock solution was prepared by adding 50 μL of 10 mg of PHE-$d_{10}$/mL of MeOH to 1 L of a 0.03 M $NaN_3$ solution. The vials were shaken horizontally (120 rpm; 37 days; 20 ± 2 °C). POM strips were extracted as described previously.

**Desorption Kinetics.** Rapidly desorbing native PAH fracions were determined using a single 24 h Tenax extraction (19). Extraction with Tenax was used because of its ability to serve as an infinite PAH sink (keeping the aqueous concentration close to zero) and almost instantaneous sorbate sorption (14). Triplicate smelter samples (0.25–0.4 g dry weight), a 0.03 M $NaN_3$ solution (70 mL), and Tenax (0.5 g) were brought in 120 mL separation funnels. After horizontal shaking (120 rpm; 24 h) at room temperature, Tenax beads were separated from the slurry, washed (70 mL of 0.03 M $NaN_3$), and extracted with 10 mL of hexane containing 100 ng of ANT-$d_{10}$ (internal standard). For two samples, (scrubber neutralized and lagoon), the 24 h extraction time was checked by determining long-term desorption curves using sequential Tenax extraction for 60 days (14). The procedure is identical to the previous description, except for the amount of Tenax added (0.25 g). The Tenax was replaced after 6, 24, 48, 120, 216, 360, 720, and 1400 h.

**Quantification.** Carbon levels were determined using a CHN element analyzer (ECS 4010, Costech Analytical Technologies, Valencia, CA). PAH were identified and quantified using GCMS, in single-ion monitoring mode (ThermoFinnigan Trace GC/Polaris Q MS, Thermo Electron Corporation, Waltham, MA). Prior to analysis, all extracts (in hexane) were dried over $Na_2SO_4$, cleaned on ENVI-18 solid phase columns (Supelco, Bellefonte, PA), and concentrated to <1 mL under $N_2$ flow in an ice bath.

## Results and Discussion

**Characterization.** Varying levels of TOC were observed (2.6–28%, Table 1); however, the ratios of BC to TOC were relatively constant (25–48%, Table 1) and at the high end of the interval reported for 90 soil and 300 sediment samples (10), similar to levels reported for coal soot (21%), activated carbon (21–42%), and diesel soot (46–68%) (12, 16, 20). For other soot materials, like traffic soot, oil soot, and wood soot, thermal oxidation resulted in almost complete sample loss (20). On the other hand, N-containing compounds have shown the tendency to char, resulting in artificially high BC contents (16). However, the total organic nitrogen (TON) levels in our samples were below 0.5%, limiting the risk of charring (21). Applying the CTO 375 °C method without wet chemical
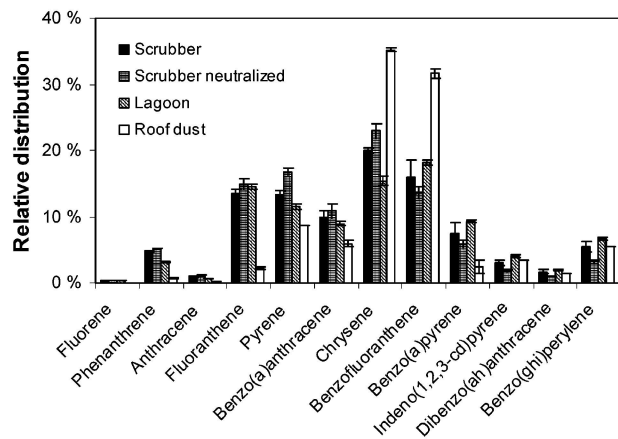
FIGURE 1. Relative distribution of total extractable content of PAH in aluminum smelter samples: scrubber, scrubber neutralized, lagoon, and roof dust.

pretreatment ($16$) resulted in 27 and 33% higher BC values for scrubber neutralized and lagoon, respectively. Given the methodological challenges with various matrices in the CTO method ($22$), this variation is considered to be acceptable.

PAH levels are generally high (0.25−0.50% sediment d.w.) with the exception of roof dust (0.05% sediment d.w.) and are dominated by four- and five-ring PAHs (Figure 1). The two samples from the wet scrubber and the lagoon sample were comparable in their relative PAH distribution; however, the roof dust sample, which had not passed the scrubber, showed a different PAH distribution pattern, with a significantly higher contribution of chrysene and benzofluoranthenes ($t$-test >95%). This might be a result of thermal/photolytical weathering on the roof resulting in the removal of the lighter compounds or the absence of coal tar condensation occurring in the wet scrubber. On a carbon-normalized basis, the PAH levels are lower in the lagoon and roof dust samples than in the scrubber samples, probably due to dilution in the environment.

**TOC−Water Partitioning.** All four samples showed high and comparable $K_{TOC}$ values despite a 1 order of magnitude variation in PAH content (Figure 2a). This is in apparent contrast with an observation for lampblack-impacted soils containing high levels of BC, where a strong reduction in distribution coefficients at higher PAH levels was found ($23$) and attributed to soot surface coverage by a PAH−oil coating.

The presently observed $K_{TOC}$ values for aluminum residues are up to 2 orders of magnitude higher than literature ones calculated using a frequently used linear free energy relationship (LFER; Supporting Information Table S2 and ref $24$). Similar observations have been reported for sediment samples from anthropogenically influenced sites containing significant amounts of BC ($10$, $13$) and/or tar pitch ($25$). This behavior is attributed to the strong sorptive behavior of BC and pitch. The $K_{TOC}$ values found here are similar to the values reported for native four- to six-ring PAH in coal soot ($20$). Even higher values have been reported for diesel soot (Figure 2b) ($20$, $26$). High partition coefficients have also been reported for PAH in weathered oil and coal tar pitch ($25$, $27$, $28$). These literature values are within the 95% confidence interval of the partition coefficients reported for the aluminum smelter residues studied here (Figure 2b).

**Sorption of Spiked Deuterated Phenanthrene.** To study whether aluminum residues exhibit nonlinear sorption characteristics typical of BC-dominated adsorption ($10$) or linear ones typical of partitioning/absorption into a semisolid tar phase ($28$, $29$), sorption isotherms for PHE-$d_{10}$ were determined for two of our samples (scrubber neutralized and lagoon). Analysis of the carbon-normalized data using the Freundlich isotherm ($C_{AL} = K_F C_W{}^{n_F}$, where $n_F$ is the
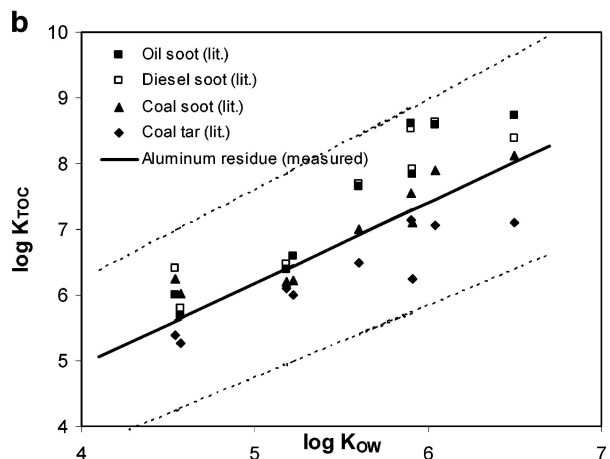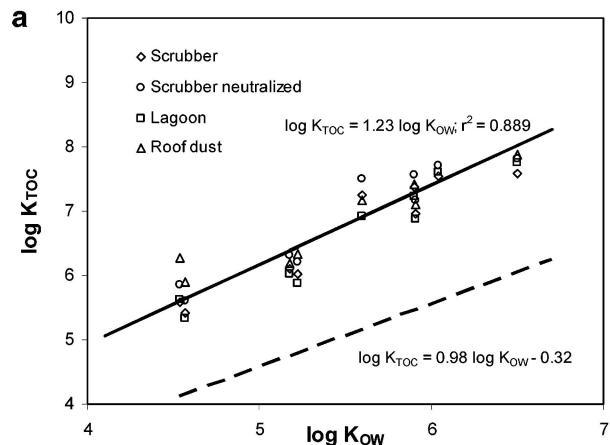


FIGURE 2. Observed $K_{TOC}$ values for aluminum smelter residues (a) as compared to calculated values using a frequently used LFER ($24$) and (b) as compared to literature values for other carbonaceous phases ($20$, $28$). The solid line indicates linear regression for the presently observed aluminum smelter residue data (dotted lines; 95% confidence interval).
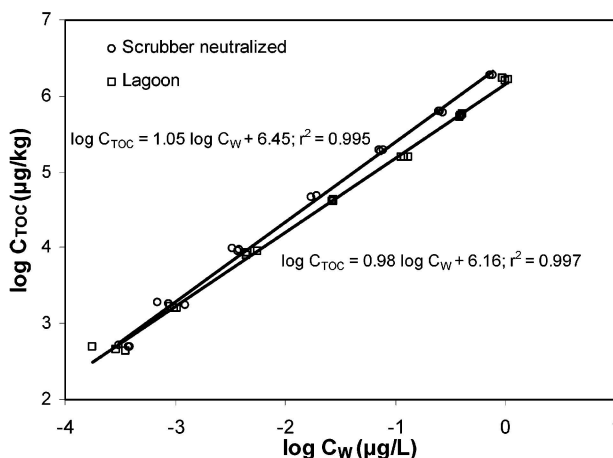


FIGURE 3. Sorption isotherms of phenanthrene-$d_{10}$ on aluminum smelter residues. Scrubber neutralized (O) and lagoon (□).

Freundlich nonlinearity coefficient, $K_F$ is the Freundlich sorption coefficient, and $C_{AL}$ is the solid concentration in the Al smelter residue) revealed $n_F$ values of 1.05 ± 0.02 and 0.98 ± 0.01 for lagoon and scrubber neutralized, respectively (Figure 3). $K_F$ was 6.45 ± 0.04 and 6.16 ± 0.03 [($\mu g/kg)/(\mu g/$L$)^{n_F}$], respectively. The sorption isotherms were not significantly different for the two samples ($t$-test >95%), and the whole data set can be described with a linear isotherm ($n_F$ = 1), giving a $K_{TOC}$ value of 6.29 ± 0.03 (L/kg; $r^2$ = 0.99). The
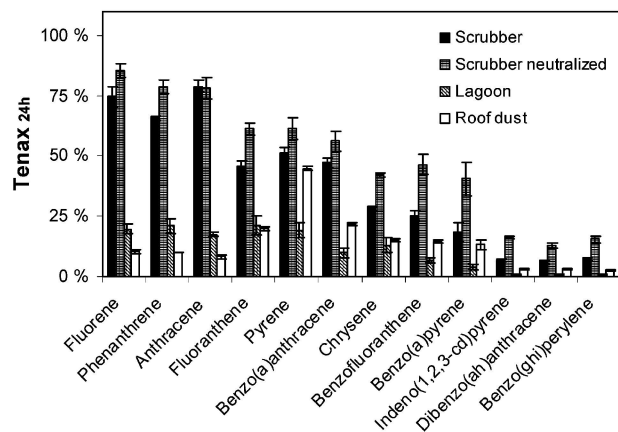
**FIGURE 4. Fraction of total PAH content desorbing in 24 h Tenax extraction.**

linear sorption behavior of PHE-$d_{10}$ sorption over a wide concentration range ($C_W/S = 10^{-7}$ to $10^{-3}$) supports a tar pitch-dominated absorption rather than a BC-dominated adsorption for the smelter residues.

**Rapidly Desorbing Fractions.** Single Tenax extraction over 24 h (Tenax$_{24h}$) showed a large rapidly desorbing fraction of PAH for fresh smelter residues (scrubber and scrubber neutralized), whereas the rapid fractions in the lagoon and roof dust samples were much lower (Figure 4).

Single Tenax extraction has been shown to give a good quantification of the rapidly desorbing fraction ($F_{rapid}$) of various organic contaminants in sediments (19), although there is some discussion concerning the length of time that should be used. Cornelissen et al. (19) suggested using twice the amount desorbed in 6 h as a measure of $F_{rapid}$. Others have used 24 or 30 h Tenax extraction for $F_{rapid}$ determination (30). To test the significance of the Tenax$_{24h}$ data obtained for aluminum residues, long-term desorption curves were established for the scrubber neutralized and lagoon sample. Quantitative data on desorption kinetics were obtained by fitting the desorption curves to first-order two- and three-compartment models (for methodological details, see Supporting Information and ref 30). The $F_{rapid}$ from the sequential extraction showed a good correlation with the Tenax$_{24h}$ data for three-ring PAH. However, for high molecular weight PAH, Tenax$_{24h}$ data deviate from both two-compartment model results (higher values), and the three-compartment model results (lower values). This discrepancy is clearer in scrubber neutralized than in the lagoon sample and can be attributed to difficulties in modeling desorption curves with a very steep initial desorption phase (Supporting Information Table S3 and Figure S2).

The presently observed rapid fractions for scrubber/scrubber neutralized of 66−79% for PHE, 51−62% for PYR, and 19−41% for BAP are high as compared to the literature values for native PAH in contaminated sediments that are in the order of 8−29% for 100 samples (30). The Tenax$_{24h}$ fractions for lagoon and roof dust, however, are in the same range as literature values for contaminated sediments. Recently, desorption kinetics of native PAH for soot and soot-like materials has been reported (31). Traffic soot, oil soot, wood soot, coal, and charcoal showed very low rapidly desorbing fractions, especially for high molecular weight PAH. Coal soot, however, showed rapidly desorbing fractions ($F_{rapid}$) in the same order of magnitude as the Tenax$_{24h}$ data for lagoon and roof dust (31).

**Carbonaceous Sorbents.** The distinction between an AOC and a BC fraction in TOC originates from studies on environmental samples where BC and AOC were studied separately (10, 17, 26, 32). The carbonaceous material in aluminum smelter residues is of a different origin, which

limits the applicability of existing dual-mode sorption models. The samples used in the present study originate from high temperature oxidation of anodes composed of petroleum coke and tar pitch. Only in the lagoon sample was plant organic matter identified (root fragments). The fraction of TOC that could be removed from the samples using wet chemical HF pretreatment followed by chemo-thermal oxidation at 375 °C varied from 52 to 58% for scrubber, scrubber neutralized, and lagoon and 75% for roof dust. To elucidate the chemical nature of this easily oxidizable fraction, we have to consider the aluminum smelter process in more detail. In the Söderberg process, a continuous anode is supplied as a paste composed of a coke/coal tar pitch mixture (~75:25%) that is baked by the heat from the smelter (approximately 970 °C) (3). Coke has a porous structure and includes approximately 10% volatile hydrocarbons. Thus, the viscous coal tar pitch (CT) binder will probably redistribute in the voids of the coke aggregate at temperatures below 350 °C. Above 450 °C, volatile hydrocarbons are released, and a solid carbon matrix is formed during pyrolysis of the anode paste as a result of cracking, dehydrogenation, and polymerization (3). In spite of its carbonaceous character at the molecular scale, the overall carbon matrix formed will have an amorphous macrostructure at temperatures below 1000 °C (3), which can explain the deviation from BC-type sorption behavior that we observed. CT vapors from the process are partly released to the atmosphere and partly collected and treated in the wet scrubber. Studies on PAH partitioning between coal tar (CT) and water show linear partitioning coefficients ($K_{CT}$) that vary considerably among different studies and sorbents reviewed by Endo and Schmidt (28). They are approximately 1 order of magnitude higher than $K_{AOC}$ values (24). Yet, these values are an order of magnitude lower than observed for smelter residues and soots (Figure 2b and Supporting Information Table S2)

To quantify the relative importance of coal tar (CT) and BC in the observed PAH sorption in aluminum smelter residues ($K_{AL}$), a dual-mode sorption model was used

$$C_{AL} = f_{CT}K_{CT}C_W + f_{BC}K_{BC}C_W^{n_{BC}} \qquad (1)$$

where $f_{CT}$ ($= f_{TOC} - f_{BC}$) and $f_{BC}$ are the mass fractions of CT and BC, respectively, $K_{CT}$ is the coal tar−water distribution coefficient (L/kg$_{CT}$), $C_W$ is the freely dissolved aqueous concentration ($\mu$g/L), $K_{BC}$ is the BC-water distribution coefficient [($\mu$g/kg)/($\mu$g/L)$n_{BC}$], and $n_{BC}$ is the Freundlich nonlinearity coefficient. Using mean $K_{CT}$ data from ref 28, coal soot $K_{BC}$ data from ref 20, and $n_{BC} = 0.61$ from ref 10, theoretical $K_{AL}$ values can be calculated (Supporting Information Table S2). These calculated data show a good correlation with observed $K_{AL}$ data (Figure 5).

However, this approach is limited by uncertainty factors. First, it is difficult to discern CT from BC for two reasons: (i) part of CT is resistant to oxidation at 375 °C and thus characterized as BC (25) leading to overestimation of $f_{BC}$ and (ii) possibly only part of the coal soot survives 375 °C and is thus characterized as BC, leading to underestimation of $f_{BC}$ (20). Second, the sorptive properties of BC are changed by NAPL loading (23). A CT cover on BC particles in aluminum smelter residues will probably result in less strong and less nonlinear BC sorption and thus a more significant contribution of linear sorption dominated by CT. A strong contribution of linear absorption has been observed in diesel soot at high PHE concentrations (33).

Because of the uncertainty in our BC and CT quantifications, we carried out a sensitivity analysis of our model calculations by testing $f_{BC} = 0.2f_{TOC}$ (and thus $f_{CT} = 0.8f_{TOC}$) and $f_{BC} = 0.8f_{TOC}$, respectively. This sensitivity analysis showed that assuming $f_{BC} = 0.2f_{TOC}$ (i.e., $f_{BC}$ values approximately 50% below the measured data) resulted in a good fit with the
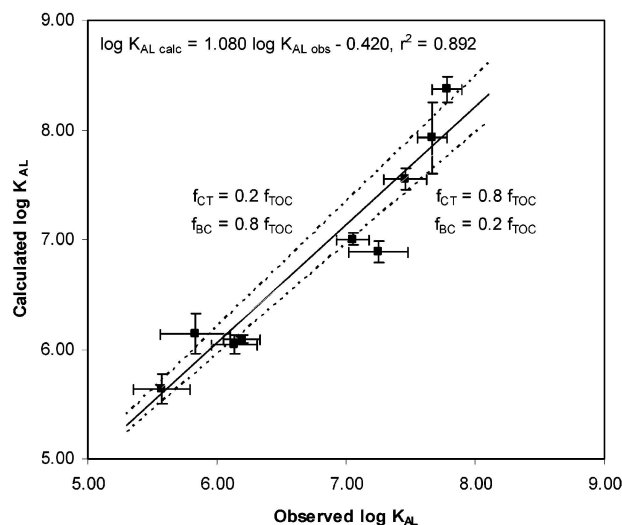
**FIGURE 5.** Correlation between calculated $K_{OC}$ values for aluminum smelter residues ($K_{AL,calc}$) based on a dual mode sorption model and observed values ($K_{AL,obs}$). Dotted lines indicate the sensitivity of the model estimates for the fraction coal tar (CT) and fraction black carbon (BC).

observed $K_{AL}$ values (log $K_{AL,calc}$ = 1.011 log $K_{AL,obs}$ − 0.11; $r^2$ = 0.908), although the estimates of the $K_{AL}$ values are not significantly improved (t-test >99%). In general, the $K_{AL,calc}$ values are not strongly sensitive to variations in $f_{BC}$ and $f_{CT}$, due to the similarity in sorption strength of CT and BC.

Although we are lacking direct evidence for the presence of a coal tar fraction in the aluminum smelter residues studied, the importance for PAH sorption of coal tar pitch is implied by several findings: (i) linear sorption isotherms for spiked PHE-$d_{10}$ and (ii) high $K_{TOC}$ values in combination with high rapidly desorbing fractions, which are not in accordance with BC-dominated sorption (30). However, the presence of a semi-solid NAPL can explain the high rapidly desorbing fraction since equilibrium partitioning, following Raoult's law, will allow complete depletion of PAH present in the NAPL matrix (29, 34).

**Environmental Risk of Al Residues.** The risk associated with sediments contaminated by aluminum smelter residues is mainly related to exposure of benthic organisms and subsequent transfer in the aquatic food chain. To assess this kind of risk, equilibrium partitioning using generic $K_{TOC}$ values has mostly been used (e.g., ref 35). However, recent research has shown that observed biota-to-sediment accumulation factors (BASF) are better explained by the available PAH content, expressed by the fraction rapidly desorbing and/or the freely dissolved concentration (36, 37). Using this approach, our results seem contradictory. On the one hand, we observed high $K_{TOC}$ values in all samples implying low aqueous activity and low actual risk. On the other hand, the scrubber and scrubber neutralized samples show a large rapidly desorbing fraction implying a high accessible quantity, particularly for three- and four-ring PAH. As pointed out by Reichenberg and Mayer (38), these two measures are principally different and give complementary information. In the aged lagoon sediments, the rapidly desorbing fractions have been strongly reduced, while the activity ($K_{TOC}$) is nearly unchanged. This might be explained by weathering of the coal tar phase, resulting in a stronger sequestration of the PAH with time. Redistribution of PAH between coal tar and BC phases can contribute to the observed sequestration and limit the long-term environmental consequences of smelter-impacted sediments.

## Supporting Information Available

Electron microscopic images and characterization data of the samples as well as sequential desorption curves and modeling results of the rapidly desorbing fractions. This material is available free of charge via the Internet at http://pubs.acs.org.

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